# Production of 5-hydroxymethylfurfural from glucose using aluminium doped MCM-41 silica as acid catalyst

Ignacio Jiménez-Morales, Mercedes Moreno-Recio, José Santamaría-González, Pedro Maireles-Torres*, Antonio Jiménez-López

*Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Campus de Teatinos, 29071 Málaga, Spain*

## ARTICLE INFO

## ABSTRACT

Mesoporous aluminium doped MCM-41 silica catalysts were prepared by a sol–gel method in two reaction steps (acid and alkaline hydrolysis) from joint hydrolysis of tetraethylortosilicate (TEOS) and aluminium triisoproxide, using n-dodecylammonium chloride as surfactant, at room temperature, and subsequent calcination at 550 °C. Two solids with different Si/Al molar ratios (5 and 10) were synthesized, which possess high specific surface area and acidity, with both Brönsted and Lewis acid sites. By using a biphasic water/MIBK as reaction medium and a 30 wt.% of the 10Al-MCM catalyst with respect to the substrate weight (glucose), 87% of glucose conversion and 36% of HMF yield were achieved at 195 °C after 150 min of reaction time. The reaction is quite selective toward HMF, since only fructose was detected as by-product, but neither levulinic acid nor furfural were found. Moreover, the use of a sodium chloride aqueous solution (20 wt.%) and MIBK ameliorates the partition coefficient between the organic and the aqueous phases up to 1.9, leading to an enhancement of the glucose conversion and HMF yield, attaining values of 98% and 63%, respectively, in a time as short as 30 min. The catalytic performance of this acid solid, associated to the presence of strong acid sites, is well maintained after three catalytic cycles.

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## 1. Introduction

The continuous increasing in energy consumption, diminishing fossil fuel reserves and the growing environmental concerns have increased the interest in renewable resources. Biomass is a green renewable energy source that takes advantage of its abundance, sustainability, environmentally friendly and wide distribution in nature [1,2]. On the other hand, it is a source of carbohydrates that can be transformed into biofuels and a large spectrum of high value-added chemicals. In this sense, glucose derived from biomass is an important feedstock for the production of green platform chemicals like 5-hydroxymethylfurfural (HMF), with numerous industrial applications. Thus, it can be converted to 2,5-furandicarboxyl acid, 2,5-dihydroxy methyl-furan and 2,5-bis(hydroxymethyl) tetrahydrofuran. All of them are building blocks to produce polyesters, and other chemicals by oxidation, hydrogenation, hydrogenolysis, aldol condensation, etc. [3,4].

Different catalytic systems have been evaluated for the HMF preparation from saccharides, such as homogeneous catalysts in hot compressed water [5], metal salts in dimethylsulfoxide [6], ionic liquids [7], lanthanide salts in ionic liquids [8] and metallic salts with mineral acids [9]. The state of the art of the catalytic dehydration of C6 carbohydrates has been reviewed recently by Wang et al. [10]. It is well known that the use of mineral acids as catalysts in this reaction involves several problems such as toxicity, corrosion, catalyst waste, use of large amount of catalyst and difficult separation operations [12]. Therefore, their replacement by solid acids is highly recommended owing to their absence of corrosiveness, environmentally friendly nature and easy separation and recovery. Several heterogeneous catalysts have been reported for HMF preparation, such as titania and zirconia under microwave irradiation [13], sulphated zirconia/alumina in DMSO [14], sulphated zirconia/titania [15], layered Zr and Ti phosphates [16], heteropolyacids [17], tungstated zirconia [18], niobic acid [19–22], among others.

On the other hand, mesoporous solids present advantages with respect to conventional porous solids when they are used as catalysts, due to their high surface area, large pore size and thermal and hydrothermal stabilities [23–25]. Moreover, the incorporation

of aluminium into the framework of mesoporous silica leads to the generation of acid sites of medium strength with potential applications as catalysts in different reactions, such as hydrocarbon isomerization, alkylation, cracking and hydrocracking, etc. [26–29]. However, the amount of tetrahedral aluminium incorporated into mesoporous silica depends on several factors, including the aluminium source [30]. These authors have developed a sol–gel method in the presence of a surfactant to prepare Al-MCM-41 catalysts in two steps. The first one is carried out in acidic medium, which favours the hydrolysis reaction with the formation of Al-containing micelle-templated silica, and delays the condensations of products. In the second step, at basic pH, the condensation of the hydrolyzed products takes place. Moreover, this experimental approach requires soft experimental conditions, since it is performed at room temperature in a short reaction time.

In the present work, the preparation by following this synthetic method, but with the modifications introduced by Araujo et al. [31], of two catalysts with Si/Al atomic ratios of 5 and 10 is described, as well as their application in the catalytic reaction of dehydration of glucose to 5-hydroxymethylfurfural in a bi-phasic medium. Different experimental parameters, such as reaction temperature and time, loading of catalyst, reaction medium and its reusability, have been evaluated in order to find the optimal conditions to attain the maximum yield of HMF.

## 2. Experimental

### 2.1. Catalysts preparation

Mesoporous Al doped MCM-41 silica was prepared by a sol–gel method in two reaction steps (acid and alkaline hydrolysis) [30,31]. In a typical experiment, a joint solution of tetraethylortosilicate (TEOS) and aluminium triisoproxide was prepared under mild stirring, followed by the addition of n-dodecylammonium chloride hydro-alcoholic solution previously shaken for 10 min at room temperature. This solution was prepared by treating 5 g dodecylamine in 20 ml ethanol. The pH was adjusted to 2 by addition of HCl (37 wt.%). Two samples were prepared with Si/Al atomic ratios of 5 and 10. Acid hydrolysis was carried out for 90 min, under stirring. Then, pH was adjusted to 10 with aqueous ammonia (30 wt.%) to produce alkaline hydrolysis and condensation of silicate groups. Finally, the obtained gel was aged for 20 h at room temperature, under static conditions. The solid was filtered, washed with water and dried overnight at 105 °C. Later, the solid underwent solvent extraction with ethanol/HNO$_3$ 0.1 M for 4 h, followed by calcination at 550 °C for 3 h. Solids with Si/Al atomic ratios of 5 and 10 were labelled as 5Al-MCM and 10Al-MCM, respectively.

### 2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns of catalysts were obtained in a PAN analytical XíPert Pro automatic diffractometer. Powder patterns were recorded in a Bragg-Brentano reflection configuration by using a Ge (1 1 1) primary monochromator (Cu Kα$_1$) and the XíCelerator detector with a step size of 0.017° (2θ), between 10 and 70° in 2θ with an equivalent counting time of 712 s/step.

X-ray photoelectron spectra were performed using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Al

K$_\alpha$ radiation (300 W, 15 kV, 1486.6 eV) with a multi-channel detector. Spectra of samples were recorded in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1$s$ at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. All recorded spectra were always fitted using Gaussian-Lorentzian curves to more accurately determine the binding energy of the different element core levels. The modified Auger parameter of Al ($\alpha'$) was calculated using the following equation: $\alpha' = 1253.6 + KE(Al_{KLL}) - KE(Al\ 2p)$, where $KE(Al_{KLL})$ is the kinetic energy of the Auger electron of Al$_{KLL}$ and $KE(Al\ 2p)$ the kinetic energy of the photoelectron Al 2p [31].

The textural parameters were evaluated from the nitrogen adsorption–desorption isotherms at −196 °C, as determined by an automatic ASAP 2020 system from Micromeritics. Prior to nitrogen adsorption, samples were evacuated overnight at 350 °C. Pore volume and the pore size distribution were determined using the BJH method.

Temperature-programmed desorption of ammonia (NH$_3$-TPD) was carried out to evaluate the total acidity of catalysts. These were heated from room temperature to 550 °C (heating rate of 10 °C min$^{-1}$), under a helium flow (35 ml min$^{-1}$), and then maintained at this temperature for 15 min. Samples were cooling until 100 °C under a helium flow, at which ammonia adsorption is carried out. NH$_3$-TPD was performed under the same conditions used for the catalyst activation. The evolved ammonia was analyzed by on-line gas chromatography (Shimadzu GC-14A) provided with a TCD.

FTIR spectra of adsorbed pyridine were recorded on a Shimadzu Fourier Transform Infrared Instrument (FTIR-8300). Self supported wafers of the samples with a weight/surface radio of about 15 mg cm$^{-2}$ were placed in a vacuum cell greaseless stopcocks and CaF$_2$ windows. The samples were evacuated at 250 °C and 10$^{-2}$ Pa overnight, exposed to pyridine vapours at room temperature for 15 min and then outgassed at different temperatures. To determine the concentration of both types of acid sites, the extinction coefficients obtained by Datka et al., $E_B = 0.73$ cm μmol$^{-1}$ and $E_L = 1.11$ cm μmol$^{-1}$, for Brönsted and Lewis acid sites, respectively, were used [32].

### 2.3. Catalytic test

For the dehydration reaction of glucose, a two-phase reactor system, consisting in pure water/MIBK or aqueous solution of sodium chloride/MIBK, was used. MIBK was introduced to promote the dehydration reaction by shifting the equilibrium toward the formation of HMF, by extracting it immediately under stirring. In this way, HMF degradation can be avoided [1,10]. The catalytic reaction was carried out in a glass reactor of 15 ml, provided with a screw top of Teflon, in the temperature range of 155–195 °C, with a stirring rate of 600 rpm. Zero time was taken when the temperature of the reactor reached the desired value. The reaction was performed by using 50 mg of catalyst, 0.15 g of substrate in deionized water (1.5 g) and 3.5 ml of MIBK. After reaction time, this was quenched by introducing the reactor in a cooled water bath; the liquid phases were separated and filtered, and the analysis of products was done in both phases. Glucose conversion and product selectivity were calculated according to the following equations:

$$\text{Glucose conversion (wt.\%)} = \frac{(\text{mass of starting glucose} - \text{mass of remaining glucose})}{\text{mass of starting glucose}} \times 100,$$

$$\text{Product selectivity (mol\%)} = \frac{\text{moles of produced product} \times 100}{\text{moles of glucose reacted}},$$

**Table 1**
XPS data of aluminum doped mesoporous MCM-41 silica catalysts.

| Sample | Binding energy (eV) | | | Si/Al molar ratio | $\alpha'_{tetrahedral}$ Al(III) (eV) | $\alpha'_{octahedral}$ Al(III) (eV) |
|--------|------|------|------|-------------------|-------------------------------|------------------------------|
| | Al 2p | Si 2p | O 1s | | | |
| 10Al-MCM | 75.0 | 103.3 | 532.5 | 15.0 | 1458.7 | 1460.4 |
| 5Al-MCM | 74.9 | 102.9 | 532.3 | 5.4 | 1458.6 | 1460.6 |

Both the aqueous and the organic layers were analyzed by high performance liquid chromatography (HPLC), by using a JASCO liquid chromatograph equipped with a quaternary gradient pump (PU-2089), a multiwavelength detector (MD-2015), autosampler (AS-2055), column oven (co-2065) using a PHENOMENEX LUNA C18 reversed-phase column (250 mm × 4.6 mm, 5 μm) and a PHENOMENEX REZEX RHM-Monosaccharide H$^+$ (8%) (300 mm × 7.8 mm, 5 μm). The disappearance of glucose was monitored using a refractive index detector while the HMF production was monitored using a UV detector. Glucose conversion and HMF selectivity were calculated using the volumes of aqueous and organic phases used in the reaction. The solvents were filtered through a 0.45 μm filter and degassed with helium prior use. Methanol (flow rate 0.5 ml min$^{-1}$) and water (flow rate 0.6 ml min$^{-1}$) were used as mobile phases in LUNA C18 and REZEX RHM columns, respectively. Injection volumes were of 6 μl, and the columns temperature was held constant at 80 °C. All samples were dissolved in methanol (LUNA C18) or water (REZEX RHM).

## 3. Results and discussion

### 3.1.1. Catalysts characterization

The low-angle powder XRD patterns of both Al-MCM catalysts, after calcination at 550 °C, exhibit a broad peak centred at $2\theta = 3°$ corresponding to (1 0 0) reflection planes in a hexagonal arrangement (Fig. 1), which is less defined for the catalyst with a Si/Al molar ratio of 5. The XRD data can be indexed to a hexagonal lattice with a $d_{100}$ spacing ranging between 2.7 and 3.1 nm, corresponding to an average unit cell parameter $a_0$ of 3.4 nm, according to the formula $a_0 = 2d_{100}/\sqrt{3}$. On the other hand, in the high angle region (inset of Fig. 1), they only show typical broad bands associated to the amorphous silica walls, without any diffraction peak pointing out the presence of crystalline Al$_2$O$_3$, even for high aluminium content (5Al-MCM).

Surface information of these mesoporous solids has been deduced from X-ray photoelectron spectroscopy data (Table 1). The binding energy (BE) values for the Si 2p and O 1s are in the ranges 102.9–103.1 and 532.3–532.5 eV, respectively, which are characteristic of these elements in silica, whereas the value for O 1s also appears in alumina. The BE of Al 2p at 74.9 eV matches well with that reported by Pashutski et al. for this element in compounds with compositions such as Al$_x$O$_y$, where aluminium is less oxidized than in Al$_2$O$_3$ [33]. However, the surface Si/Al atomic ratio for the 10Al-MCM solid is higher than that obtained by EDX analysis (10.1), whereas that of 5Al-MCM is very close (5.7 by EDX).

In order to get insights into the chemical environment of aluminium in these compounds, the Auger parameter ($\alpha'$) has been determined, since it depends on the Al coordination. Thus, $\alpha'$ values higher than 1461.0 eV are typical of octahedral Al, whereas for tetrahedral Al is lower than 1460.4 eV [34]. All the Al KLL Auger spectra exhibit a peak at 1383.7 eV and a shoulder at 1385.5 eV, whose intensity increases with the aluminium content (Fig. 2). The $\alpha'$ parameters have been calculated and the corresponding values are compiled in Table 1. All the catalysts have two $\alpha'$ values for Al, one at 1458.7 eV typical of tetrahedral Al, and another one at 1460.6, which is characteristic of Al with octahedral

coordination. Therefore, it can be deduced that a fraction of aluminium is incorporated during the synthesis step in the siliceous structure adopting tetrahedral coordination, but there also exists octahedral aluminium located on the surface of pores. The amount of octahedral aluminium is higher for the 5Al-MCM, as expected, although its amorphous nature makes difficult to be detected by XRD. However, this octahedral aluminium located preferentially on the pore walls may be responsible of the X-ray scattering leading to the broadening of its low-angle diffraction peak (Fig. 1). Therefore, similar to microporous zeolites, it can be thought that surface tetrahedral aluminium can confer acidic properties to these catalysts.

The textural parameters of these catalysts were obtained from N$_2$ adsorption–desorption isotherms at −196 °C, and the corresponding values are gathered in Table 2. Both solids exhibit similar
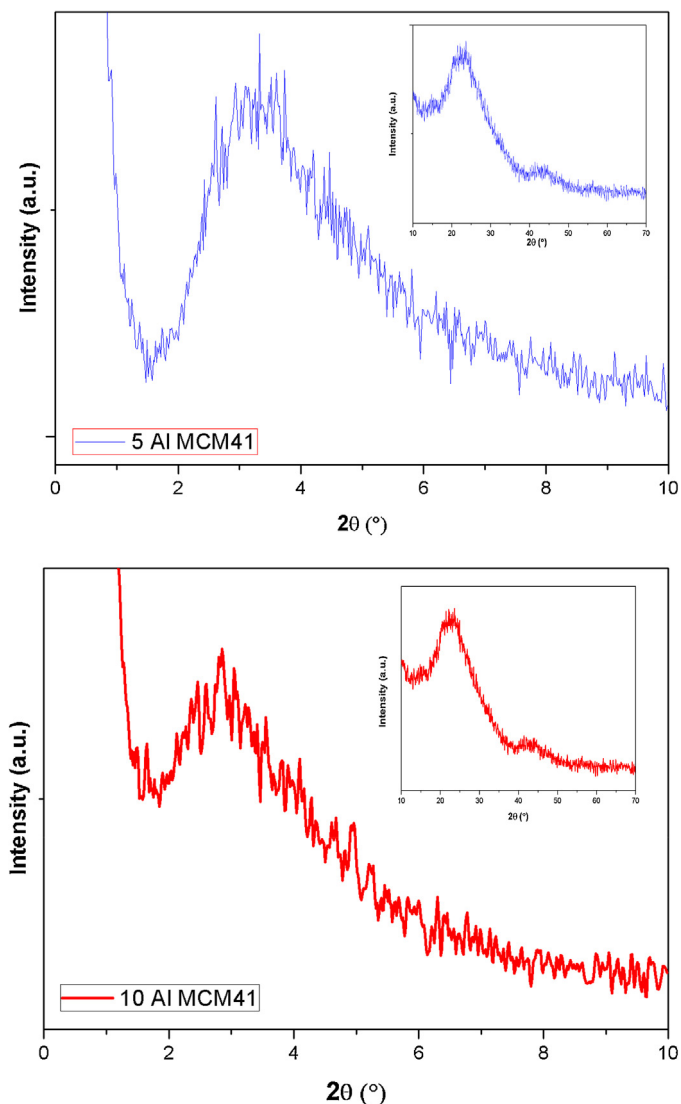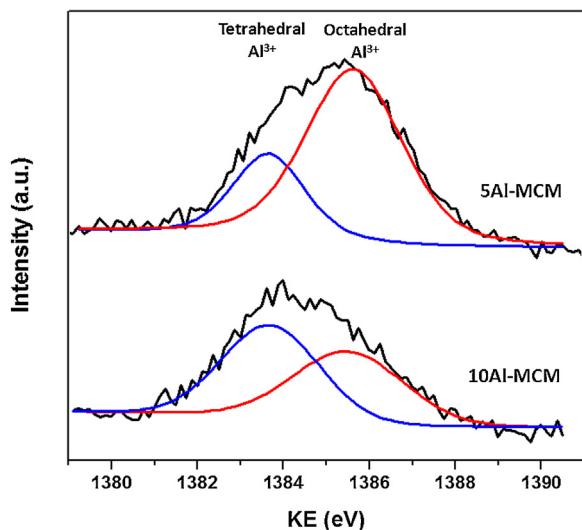


**Fig. 1.** XRD patterns at low angle and high angle (inset) of xAl-MCM catalysts.
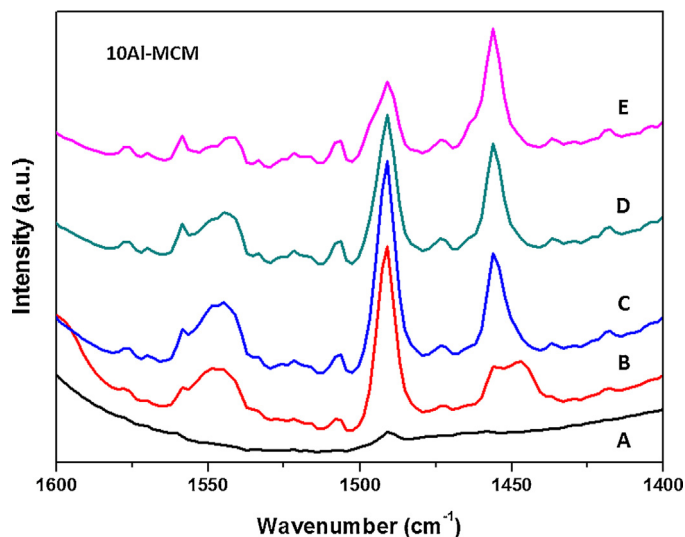
**Table 2**
Textural properties and acidity data of xAl-MCM catalysts.

| Sample | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_p$ (cm$^3$ g$^{-1}$) | $V_{micropores}$ (cm$^3$ g$^{-1}$) | Acidity (µmol NH$_3$ g$^{-1}$) | Strong acidity (µmol NH$_3$ g$^{-1}$) |
|---|---|---|---|---|---|
| 10Al-MCM | 587 | 1.33 | 0.11 | 528 | 295 (56%) |
| 5Al-MCM | 733 | 1.54 | 0.25 | 956 | 363 (38%) |



**Fig. 2.** Auger spectra of xAl-MCM catalysts.



**Fig. 4.** FTIR spectra of adsorbed pyridine on 10Al-MCM, after desorption at different temperatures: (A) without pyridine, (B) room temperature, (C) 100 °C, (D) 200 °C and (E) 300 °C.

N$_2$ isotherms (Fig. 3), belonging to the Type IV in the IUPAC classification, typical of mesoporous solids. However, there is an important increase of the adsorbed volume at high relative pressure, pointing out the existence of large size pores. The BET surface area increases with the amount of aluminium incorporated to the siliceous framework, from 587 to 733 m$^2$ g$^{-1}$ for 10Al-MCM and 5Al-MCM, respectively, which could be justified by the presence of amorphous alumina in the pores with a microporous texture. This fact could be supported by the high micropore volume shown by the 5Al-MCM catalyst, which has a higher fraction of octahedral aluminium (Table 2). The pore size distribution (inset Fig. 4)

consists of a broad band with a maximum at 1.1 nm, extending from 1.0 until 2.5 nm.

Total acidity of these mesoporous aluminium doped MCM-41 silicas, as measured by NH$_3$-TPD, is high (Table 2). Thus, 5Al-MCM exhibits the highest total acidity (956 µmol NH$_3$ g$^{-1}$), perhaps due to the excess of amorphous alumina deposited on the mesopores; however, the 10Al-MCM catalyst is also a strong acidic solid since 56% of the total ammonia molecules were desorbed at temperatures above than 300 °C, whereas this value for 5Al-MCM catalysts
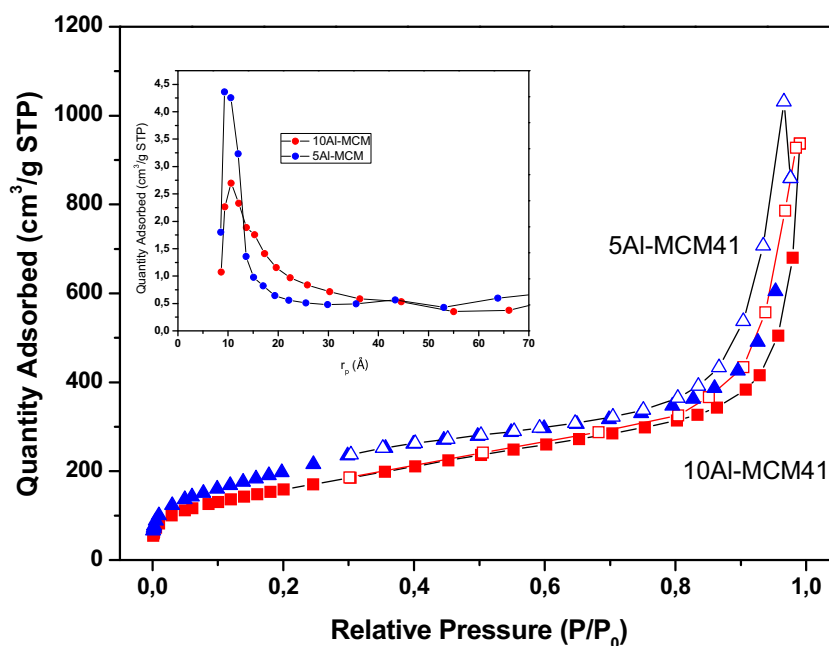


**Fig. 3.** Adsorption–desorption isotherms of N$_2$ at −196 °C of xAl-MCM catalysts and the corresponding pore size distributions (inset).
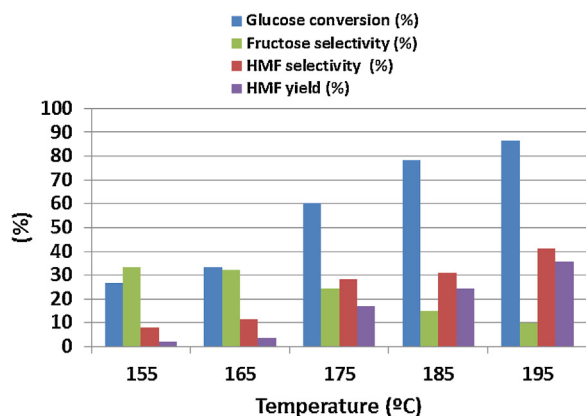
**Fig. 5.** Effect of the reaction temperature on the dehydration of glucose on 10Al-MCM. *Reaction conditions*: time = 150 min, catalyst weight: 50 mg, glucose:catalyst weight ratio = 3:1, water/MIBK (3:1 v/v) = 5 ml.
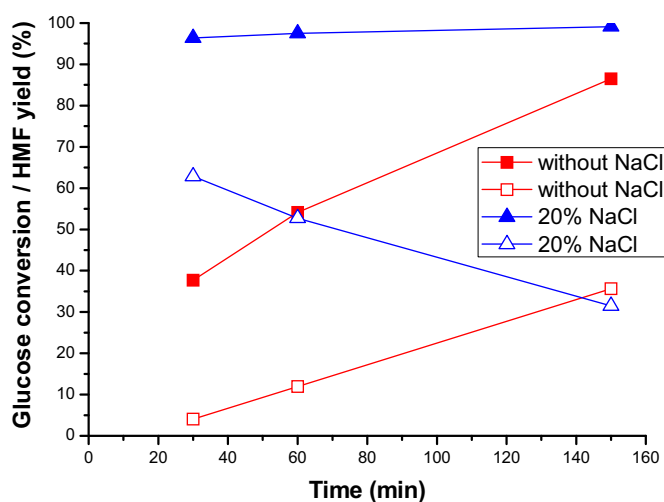
is only 38%. Nevertheless, both samples may be considered as acid solids.

The acidity study of these catalysts was completed by using adsorption of pyridine coupled to FTIR spectroscopy. The corresponding FTIR spectra (Fig. 4) show the presence of both types of acid sites, as inferred from the intense bands at $1450\,cm^{-1}$ and $1550\,cm^{-1}$ due to Lewis and Brönsted acid sites, respectively. The determination of the concentration of these acid centres, after evacuation at different temperatures, corroborates that both catalysts are strong acid solids, especially the 10Al-MCM catalyst, since an important fraction of pyridine bonded to both types of acid sites still remained even after evacuation at 300 °C (Table 3).

### 3.2. Catalytic study

Mesoporous Al-MCM-41 silicas have been evaluated as acid catalysts in the dehydration of glucose to HMF. Owing to HMF is not stable in water, a biphasic system, consisting in water-MIBK, was employed. The reaction was performed by using 50 mg of catalyst, 0.15 g of glucose in 1.5 g of deionized water (10 wt%), 3.5 ml of MIBK and 150 min as reaction time. This solvent has been successfully assayed in this reaction by other authors [1], since it is a suitable extracting agent for HMF, shifting the equilibrium toward the formation of this desired product. On the other hand, HMF degradation and its possible reaction with the intermediates from glucose to give soluble polymers and humins or acetalization with glucose can be avoided [1,10]. These secondary reactions can greatly decrease the HMF yield.

Firstly, the influence of the temperature on the catalytic reaction has been evaluated by using the 10Al-MCM catalyst. Fig. 5 reveals that glucose conversion greatly depends on the reaction temperature, especially for temperatures above 165 °C. At 195 °C, the glucose conversion achieves a maximum value close to 87%. Among the reaction products, only fructose and HMF were detected, although soluble polymers and humins are also formed because the

**Table 3**
Acidity data, as deduced from pyridine adsorption coupled to FT-IR spectroscopy.

| Evacuation temperature (°C) | 5Al-MCM | | 10Al-MCM | |
|---|---|---|---|---|
| | $C_B$ ($\mu mol\,g^{-1}$) | $C_L$ ($\mu mol\,g^{-1}$) | $C_B$ ($\mu mol\,g^{-1}$) | $C_L$ ($\mu mol\,g^{-1}$) |
| Room temperature | 127 | 61 | 252 | 123 |
| 100 | 129 | 64 | 256 | 125 |
| 200 | 103 | 65 | 198 | 113 |
| 300 | 46 | 68 | 114 | 102 |



**Fig. 6.** Evolution of glucose conversion (solid symbols) and HMF yield (open symbols) as a function of the reaction time on 10Al-MCM, in the presence (20 wt%) and absence of NaCl. *Reaction conditions*: temperature = 195 °C, mass of catalysts = 50 mg, glucose:catalyst weight ratio = 3:1, water/MIBK (3/1, v/v) = 5 ml.

catalyst becomes brown after 15–20 min of reaction; moreover, the sum of HMF and fructose doesn't match the glucose converted. The formation of fructose implies the presence of Lewis acid sites in this catalyst, as was inferred from pyridine adsorption coupled to FTIR spectroscopy. It has been proposed that glucose isomerization to fructose takes place on these Lewis acid sites, and then fructose is dehydrated to HMF. This transformation is easy even at the lowest reaction temperature studied (155 °C), where the maximum of fructose (33% selectivity) was found. As temperature rises, the selectivity to fructose decreases due to its transformation into HMF, especially at the highest temperature where the amount of fructose detected was very small (10% selectivity). However, the existence of a high concentration of Brönsted acid sites on this 10Al-MCM catalyst could also favour the direct transformation of glucose to HMF. The maximum HMF yield (36%) was achieved at 195 °C. Besides, levulinic acid was not detected among the reaction products, revealing that the acid sites present on the catalyst surface are not enough strong to produce the HMF hydration [7]. This behaviour has been previously observed by Carlini et al. [35] in their study of fructose dehydration to HMF, where the rehydration of HMF to give levulinic acid and formic acid was not found. Moreover, this was verified by putting in contact HMF with the same amount of catalyst, at 195 °C during 150 min, in the same biphasic system. The absence of levulinic acid demonstrated that 10Al-MCM is unable to rehydrate HMF.
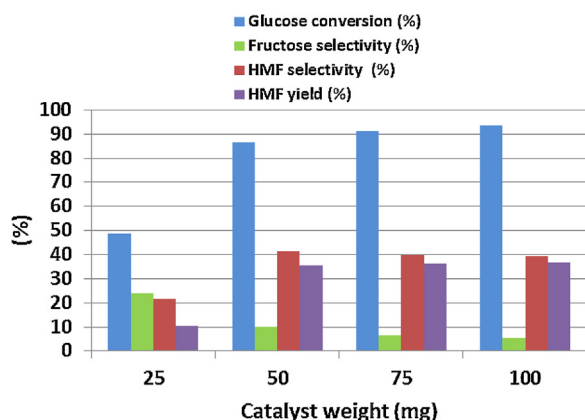
However, only 91% of HMF was recovered, being a 9% of HMF transformed in other substances different from humins, such as soluble polymers or aldol condensation products, since the colour of the catalyst does not changes. However, it has been demonstrated that humins can be formed from HMF, from 2,5-dioxo-6-hydroxy-hexanal, which is formed by hydration of HMF, by a mechanistic route different from that leading to levulinic acid and formic acid formation [11]. From these results, 195 °C was selected as the reaction temperature to evaluate the effect of other experimental parameters.

The kinetic study reveals that glucose conversion and HMF yield increase linearly with the reaction time till 150 min, where maxima values are attained (Fig. 6). A longer reaction time doesn't improve the catalytic performance, possibly as a consequence of the deposition of insoluble polymers on the active sites, thus impeding their participation in the catalytic reaction.

The study of the influence of the catalyst loading (Fig. 7) points out that, by increasing from 25 to 50 mg, the glucose conversion
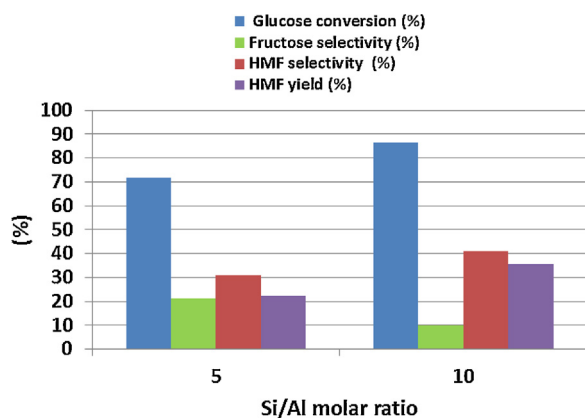
**Fig. 7.** Conversion of glucose and yield of HMF as a function of the catalyst loading. *Reaction conditions*: temperature = 195 °C, reaction time = 150 min, water/MIBK (3/1, v/v) = 5 ml.



**Fig. 9.** Influence of the addition of NaCl on the catalytic activity. *Reaction conditions*: temperature = 195 °C, time = 30 min, mass of catalysts = 50 mg, glucose:catalyst weight ratio = 3:1, water/MIBK (3/1, v/v) = 5 ml.
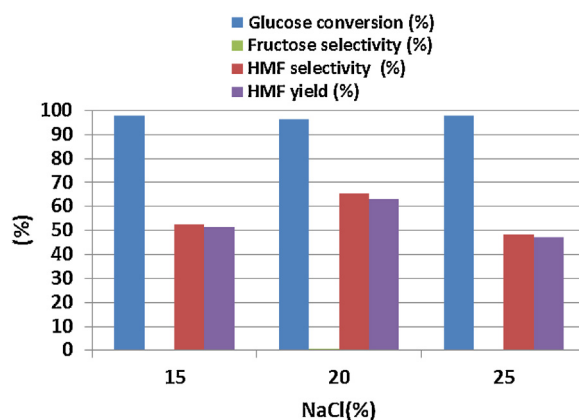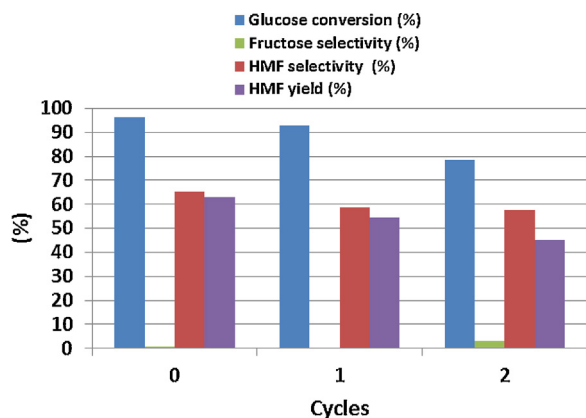
is almost twice, but higher catalyst amounts only give rise to a moderate amelioration of the glucose conversion, but this hardly results in higher HMF yields. This behaviour can be justified by the high amount of humins formed in the aqueous medium, which are deposited on the catalyst surface, covering active sites and leading to its partial deactivation.

Once the optimal conditions have been established, the 5Al-MCM catalyst has been also tested. The results displayed in Fig. 8 show that its catalytic activity is lower than that of 10Al-MCM, with only 21% of HMF yield, in spite of its higher acidity. The existence of a higher amount of strong acid sites, of both Brönsted and Lewis types, on the 10Al-MCM catalyst could explain this catalytic performance. On the other hand, the presence of amorphous alumina in the 5Al-MCM solid, possibly with acid sites of low strength, could block the pores where the most acidic centres are located, thus leading to a reduced catalytic activity.

In order to improve the HMF yield, the influence of other variables, such as the water/MIBK ratio and the addition of NaCl to the reaction medium, was tested. Thus, the use of a higher amount of MIBK (until 6.5 ml) barely modifies the glucose conversion and HMF selectivity. However, a very positive effect was observed by using a sodium chloride aqueous solution (15–25 wt.% NaCl), because glucose conversion enhanced until values close to 98% and the HMF yield attained 63% when the salt concentration was 20 wt.%, instead of pure water (Fig. 9). These data can be justified by the modification of the partition coefficients of HMF between the aqueous and organic phases, reaching values as high as 1.9 and 2.2 for

a sodium chloride solution of 20 and 25 wt.%, respectively. Moreover, these new reaction conditions not only modify the yield of HMF but also the kinetics of the dehydration process, as observed in Fig. 6 for a 20 wt% of NaCl. Thus, a reaction time longer than 30 min leads to a decrease in the HMF yield, being a half of this when the reaction time is 150 min. Therefore, long reaction time favours the formation of soluble polymers and humins, drastically reducing the yield of HMF. Even when the sodium chloride solution used was 25 wt.%, a maximum yield of HMF (62%) was attained with only 15 min of reaction time, confirming that longer reaction times lead to a decrease of the HMF yield.

The positive effect of salt addition on the HMF yield has been previously observed by Dumesic group, and it was explained by the salting-out effect that NaCl induces on the extracting solvent, due to the alteration of the intermolecular forces between solvents in the biphasic system [36]. Thus, the addition of a salt improves the partition coefficient, favouring the presence of HMF in the extracting phase. Moreover, the presence of an inorganic salt increases the upper critical solubility temperature of partially miscible systems, which remain as biphasic even at higher temperature. Basically, this salting-out effect consists in the aqueous solubility decreasing of certain compounds in the presence of inorganic salts, and Görgényi et al. have reported that it also depends on the magnitude of the hydrated ionic radius, mainly on the cation itself [37]. Later, Hansen et al. evaluated the influence of the addition of different salts on the catalytic dehydration of hexoses to HMF in a MIBK:H$_2$O biphasic system, and they found the best HMF yield by using chloride as anion [38]. On the other hand, Marcotullio and De Jong have proposed, in the homogeneous process of dehydration of D-xylose to furfural, that chloride ions promoted the formation of the 1,2-enediol from the acyclic form of the aldose, which undergoes subsequent acid catalyzed dehydration reactions to furfural [39].

An important factor in the developing of solid catalysts for HMF production is the catalyst reusability. This aspect was considered by recovering the solid after a catalytic run by filtration and reusing it in a new cycle without any treatment, such as washing or calcination. Fig. 10 shows that 10Al-MCM catalyst can be reutilized for three cycles without important loss of catalytic activity because the HMF yield only decreases about 7% after the first run and 10% after the second run. The partial loss of catalytic activity could be due to the blockage of some active sites by humins.

The results found in the present study are better than those reported by using crystalline ZrO$_2$ as catalyst in the dehydration of glucose in hot compressed water at 200 °C [5,40], even heating with microwaves [13]. Sulfated zirconia was also studied as catalyst in this reaction but with lesser HMF yield, since 48% was achieved



**Fig. 8.** Influence of the aluminium content on the catalytic activity. *Reaction conditions*: temperature = 195 °C, time = 150 min, mass of catalysts = 50 mg, glucose:catalyst weight ratio = 3:1, water/MIBK (3/1, v/v) = 5 ml.

**Fig. 10.** Reutilization study by using the 10Al-MCM catalyst. *Reaction conditions*: temperature = 195 °C, time = 30 min, mass of catalysts = 50 mg, glucose:catalyst weight ratio = 3:1, water/MIBK (3/1, v/v) = 5 ml; 20% NaCl.

by using a sulfated zirconia/alumina (1/1) [14]. A sulfated $ZrO_2/TiO_2$ transformed glucose to HMF and levulinic acid, reaching a HMF of 28.8% for a Zr/Ti molar ratio of 5.5 [15]. Also, the results obtained in the present work are better than those obtained by Qi et al. with sulphated zirconia calcined at 700 °C and under microwave heating at 200 °C [41]. The activity of this aluminium doped MCM silica is also better than that found by using other mesoporous catalysts previously reported, such as tantalum phosphate [42] and silica doped with zirconium [43]. The high catalytic activity of the 10Al-MCM catalyst can be justified not only by its high acidity, with both Brönsted and Lewis acid sites, and its mesoporous texture, but especially by the use of a reaction medium which facilitates the extraction of formed HMF in the reaction, thus avoiding its transformation into non desired compounds such as soluble polymers and humins.

In conclusion, aluminium doped MCM-41 silica catalysts are very effective in the dehydration of glucose to HMF due to the existence of a high concentration of acid sites, with both Brönsted and Lewis centres. When the reaction medium was water/MIBK good glucose conversion (87%) and HMF yield (36%) were obtained at 195 °C and 150 min of reaction time. The modification of the partition coefficient for HMF, by using a biphasic aqueous sodium chloride/MIBK system, which attained a value of 1.9 for solution of 20 wt.% NaCl, largely enhanced the catalytic activity leading to 98% of glucose conversion and 63% of HMF yield in a reaction time as short as 30 min. Moreover, this process is quite selective toward HMF, since no levulinic acid nor furfural were detected, and using this mesoporous acid solid with aqueous solutions of sodium chloride and short reaction time (30 min) makes environment-friendly and low cost the process of glucose conversion into HMF.

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